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Enhancement of magnetism of $Zn_{0.95}Co_{0.05}O$ films by p-type Cu^+ doping

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Abstract: $Zn_{0.95}Co_{0.05}O$ and $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ thin films were fabricated on Si (111) substrate by the reactive magnetron sputtering method at different O-Ar ratios. Detailed characterizations by X-ray diffractometry (XRD), X-ray photo-electronic spectrum (XPS), and electron paramagnetic resonance (EPR) indicate that the doped Cu ions substitute the Zn^{2+} ions in the ZnO lattice. The doped Cu ions are in Cu^+ and Cu^{2+} mixture valence states. The ferromagnetism of the $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ film increases gradually the increasing Cu^+ ions concentration. The results indicate that the increase of ferromagnetism is not owing to the magnetic contribution of Cu^+ ions themselves, but owing to the enhancement of magnetic interaction between Co ions, which suggests that p-type doping of Cu^+ ions plays an important role in mediating the ferromagnetic coupling between Co ions.
Key words: $Zn_{0.95}Co_{0.05}O$ films; $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films; magnetic semiconductors; magnetic coupling; co-doping

1 Introduction

ZnO-based diluted magnetic semiconductors (ZDMSs), are predicted as one type of the most promising candidates for realizing room-temperature magnetic semiconductors, which have potential applications in spintronics devices and magneto-opto-electronics[1]. ZDMSs usually present an n-type semiconductor with a wurtzite structure and the doped TM ions often substitute the Zn^{2+} sites in the ZnO lattice and induce n- or p-type defects. Although many experimental results showed ferromagnetism in ZDMSs, the reproducibility and consistency of the experiments were poor and the origin of the ferromagnetism in ZDMSs was not clear[2−6]. Recent experiments and theoretical calculations indicated that carriers and defects played important roles in mediating the ferromagnetic interaction between the transition metal ions in n-type DMSs[7−10]. Therefore, deliberately tuning the type and the concentration of the carriers and defects should be a promising way to improve the magnetic properties. Chemical perturbations treatment, annealing under a different ambience, and UV laser irradiation are used to adjust the carriers and defects in $Zn_{1-x}TM_xO$, and are proved effective in enhancing the ferromagnetisms [11−13].

Doping is a common method to manipulate the carriers and defects in semiconductors. Therefore, co-doping of a certain element was also used in modulating the structure and magnetic properties of $Zn_{1-x}TM_xO$[14−15]. In this work, metallic copper (Cu) is selected as a dopant because the valence state of Cu was controlled by chemical environment, which could act as a p-type or intrinsic dopant[16]. Most important of all, the magnetism of ZnCoO films is not affected by Cu co-doping because Cu-based secondary phases are nonferromagnetic[17]. In this paper, 4% (mole fraction) Cu co-doped $Zn_{0.95}Co_{0.05}O$ films were fabricated by the reactive magnetron sputtering method and the structure and magnetic properties were studied in detail. It is found the Cu^+ rather that Cu^{2+} ions plays an important role in mediating the ferromagnetic coupling between Co^{2+} ions.

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2 Experimental

$Zn_{0.95}Co_{0.05}O$ films were grown on Si (111) substrates by the direct-current (DC) reactive magnetron co-sputtering method using $Zn_{0.95}Co_{0.05}$ metal as targets. We chose 5% as the Co doping ratio because our previous work had shown the $Zn_{1-x}Co_xO$ samples had the maximal ferromagnetism at this Co-doping concentration[18−20]. The sputtering of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films, Cu-chips (purity of 99.999%) of the same sputtering area was attached on the $Zn_{0.95}Co_{0.05}$ target. Mixed plasma of Ar (with a fixed flux of 60) and O_2 was used for sputtering. The flux of O_2 varied from 6 to 15 mL/min. The base pressure before deposition was under 8×10^{-4} Pa and the working pressure during deposition was 0.85 Pa. The thickness of the grown films was about 2 400 Å. The $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films sputtered in the ambience with the O_2-Ar ratio of 15:60, 12:60, 9:60 and 6:60 were named as ZCCO15, ZCCO12, ZCCO9, and ZCCO6, respectively. The $Zn_{0.95}Co_{0.05}O$ films sputtered at the O_2-Ar ratio of 12:60 was labeled as ZCO.

The morphology of the samples were observed by an atomic force microscoper (AFM, PSIA XE-100E). The structures were characterized by using a Rigaku D/Max-2200 XRD with Cu K_α (1.54 Å) line and the chemical states of Co and Cu were characterized by a MK II XPS with Al K_α source. The magnetic properties were characterized by a LakerShore 7410 vibration sample magnetometer (VSM) at room temperature in air. EPR spectra were measured at room temperature with a Bruker ESP300 spectrometer operating the X-band frequency (9.78 GHz) and a 100 kHz field modulation. The *g*-values were determined using the relation as: $h\nu = g\mu_\beta H$, where h is the Planck constant, μ_β is the Bohr magneton, H is the magnetic field and ν is the microwave frequency measured with high precision using a frequency-meter.

3 Results and discussion

Fig.1 shows the AFM image of the $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ film. It is seen that the film has a very smooth surface with the approximate uniform nanoparticle size of 10 nm. Fig.2 shows the XRD spectra of the $Zn_{0.95}Co_{0.05}O$ and the $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films. All the films exhibit the ZnO wurtzite structure (JCPDS data files 65−3411) with *c* axis orientation are approved by XRD analysis, which suggests that the transition metal dopants are doped into the ZnO lattice. It also shows that the *c* values of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films increase with the increase of the O-Ar ratio, as shown in Fig.2(b).

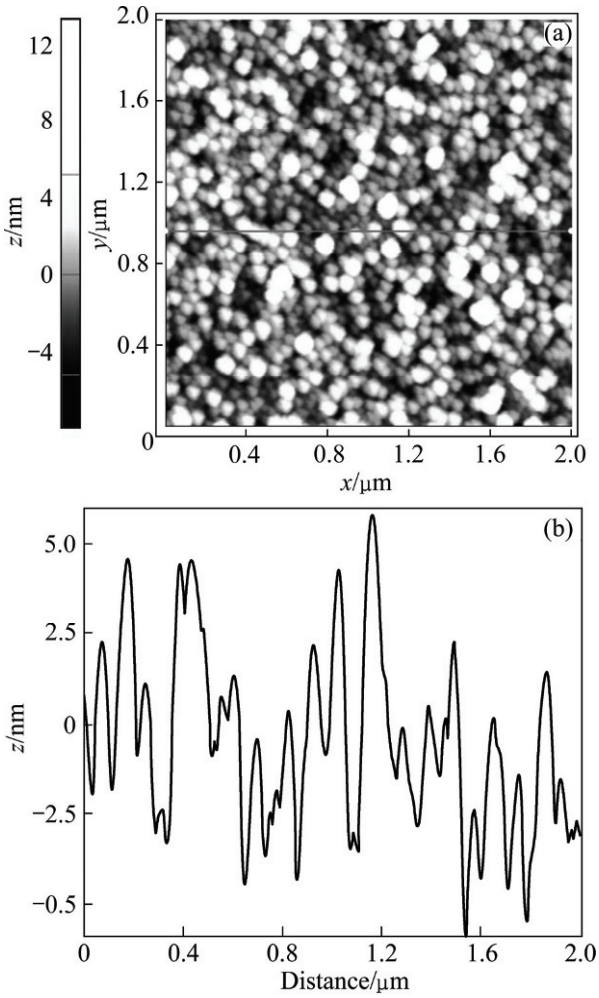

Fig.1 AFM image of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ film (a) and line profile (b)

High resolution XPS were performed to investigate the chemical state of the dopant ions in the film. The high resolution scan (Fig.3(a)) of the copper 2p peaks shows a Cu 2p3/2 peak at 932.6−933.4 eV and a Cu 2p1/2 peak at 952.6−953.4 eV. These values lie between the peak positions for Cu in Cu^+ and Cu^{2+} states[21]. Thus this suggests that Cu exists in a mixed oxidation state of Cu^+ (3d10, S=0) and Cu^{2+} (3d9, S=1/2). Fig.3(b) inset shows the Gauss fit of Cu 2p3/2 peak of sample ZCC12. According to the Gauss fit of all samples, the relationship between the Cu^+ concentration and the O-Ar ratio is shown in Fig.3(b). It clearly shows that the ratio of the Cu^+ component decreases with the increase of O-Ar ratio. It is suggested that with the decrease of oxygen partial pressure, more Cu ions turn into Cu^+ for lacking oxygen. High resolution scans of the Co 2p peak (Fig.3(c)) show the Co 2p3/2 peak at 781.5 eV and the Co 2p1/2 peak at 796.5 eV. The presence of satellite peaks at 787 and 802.5 eV confirms that Co ions exist at +2 valence and in a high-spin state within the ZnO matrix[22−23]. It is proved that the Co and Cu dopant

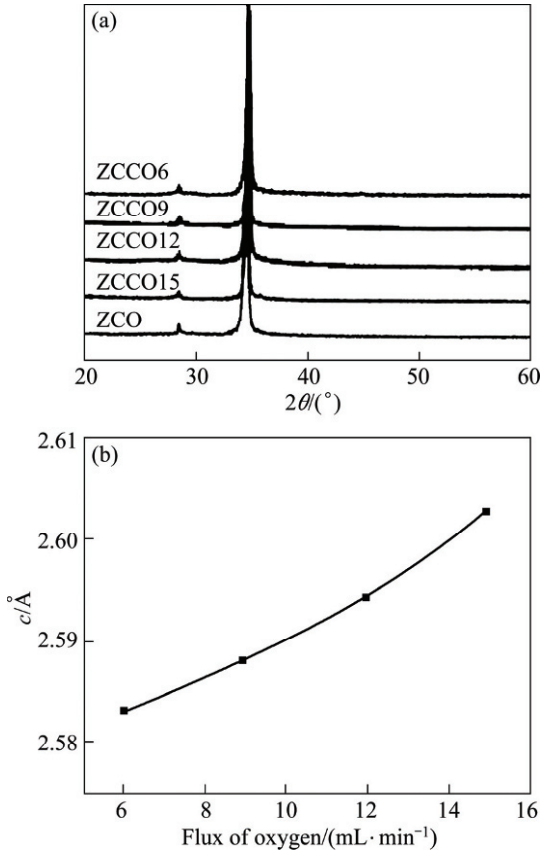

Fig.2 XRD patterns of $Zn_{0.95}Co_{0.05}O$ film and $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films prepared under different O_2-Ar ratios: (a) XRD patterns; (b) Changes of *c* values

atoms substitute Zn^{2+} in the ZnO lattice, which is consistent with the XRD results.

The mixture state of Cu ions is also proved by the EPR spectra, as shown in Fig.4. Two sorts of EPR signals observed are marked with *A* and *A′*. The *A* signal characterized by $g_{\parallel}$=2.232 and $g_{\perp}$=2.036 is attributed to the isolated Cu^{2+} ions located in the ZnO wurtzite lattice[24−25]. The higher the intensity of *A* signal becomes, the more quantity of Cu^{2+} are diffused to homogeneous positions in the film. The relationship between peak intensity of *A* signal and Cu^{2+} concentration is shown in Fig. 4(b). It is seen that the Cu^{2+} ions increase with the increase of O-Ar ratio as shown in the XPS results. Moreover, a wide *A′* signal with *g*=2.089 is observed in the ZCCO15 film. The presence of *A* signal indicates the interaction of paramagnetic Cu^{2+}, suggesting Cu^{2+} in the form of clusters. This suggests that the Cu ions are mainly in Cu^{2+} state and they have the tendency to congregate under the O-rich condition.

Fig.5 shows the VSM results, in which all the samples exhibit weak ferromagnetism. The saturation magnetisms of the $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films increase with the decrease of O-Ar ratio. The $Zn_{0.90}Co_{0.05}O$ film has the magnetism of 5.1 emu/cm^3, which is smaller than that of the ZCCO6 film (12.6 emu/cm^3), ZCCO9 (6.7 emu/cm^3) and ZCCO12 (8.8 emu/cm^3), but larger than that of the

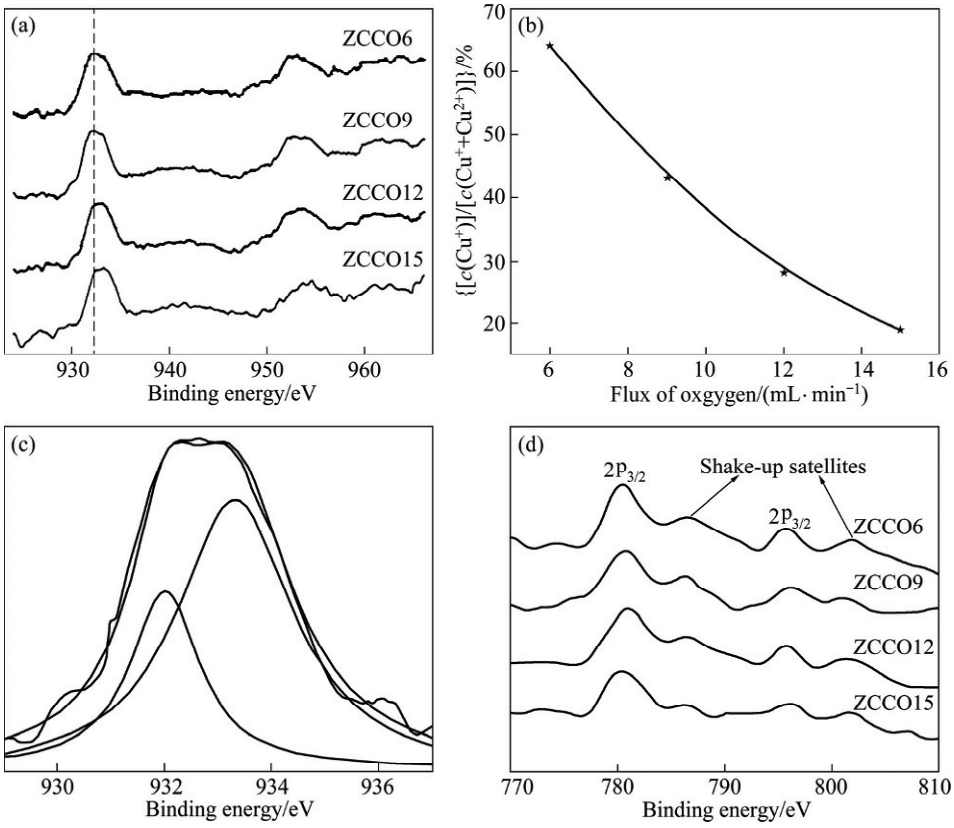

Fig.3 High resolution XPS spectra of Cu (a), relationship between Cu^+ concentration and O-Ar ratio (b), Gauss fitting curves of Cu 2p3/2 peak of sample ZCC12 (c) and high resolution XPS spectra of Co (d)

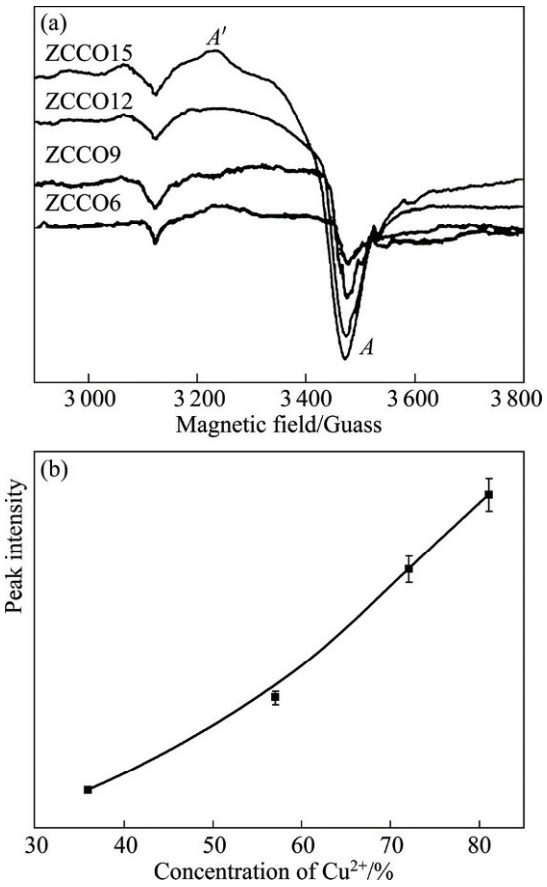

Fig.4 EPR spectra of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films (a) and evolution of *A* peak intensity of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films with different Cu^{2+} concentrations (b)

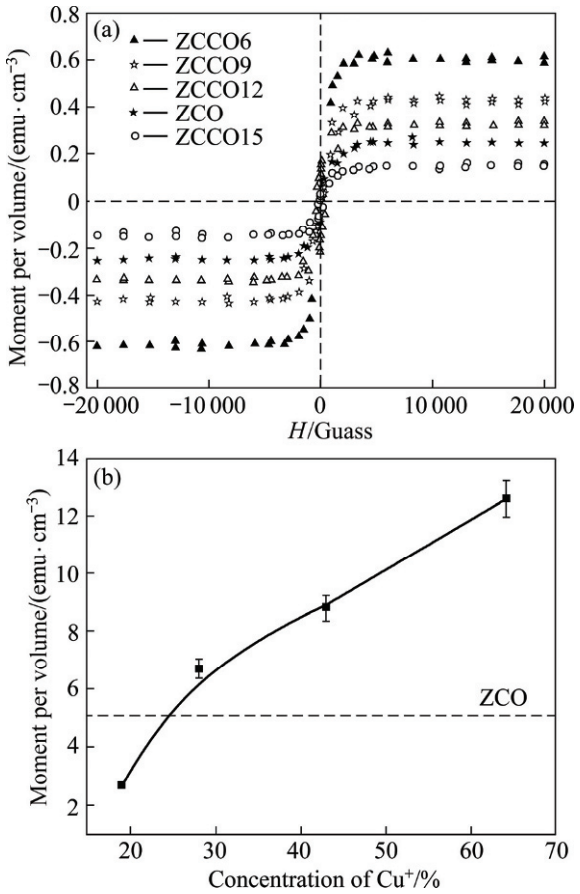

Fig.5 *M*—*H* curves of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films (a) and evolution of magnetizations of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films with different Cu^{+} concentrations (b)

ZCCO15 film (2.7 emu/cm^3). The VSM results and the structure characterizations indicate the ferromagnetic of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films are closely related to the chemical state of Cu ions. When the oxygen partial pressure is relatively low (O-Ar ratio<12:60), the Cu ions are mainly in +1 valence, and only in this case, the co-doping of Cu should be p-type, and the ferromagnetism increases. This is consistent with the theoretical prediction by simulation[26−27].

COEY et al[28−29] proposed that in ZnO or SnO_2 based DMSs, shallow donor electrons bound to defects formed bound magnetic polarons (BMPs) and created a spin-split impurity band. The BMPs or spin-split impurity band played the critical roles in mediating the ferromagnetic interaction between transition metal ions. The accepter defects, such as $Cu_{Zn}^{/}$ in the +1 valence (Zn^{2+} ion substituted by Cu^{+} ion) state and V_{Zn}, in $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ films can bind donor electrons to form BMPs, which mediates the ferromagnetic coupling between Co^{2+} ions. The concentration and action sphere of BMPs are affected by not only the n-type carriers in the ZDMSs but the p-type defects induced by Cu doping. When no Cu ions doped, although the concentration of n-type carriers is high, the concentration of accepter defects is relatively low, and thus the effective area of BMPs is limited. This is similar to the results of TIWARI et al[30], showing that ZDMSs only present ferromagnetism when the n-type carrier concentration is lower than a critical value. When Cu ions are p-type doped, the accepter defects, as well as the BMPs increase. This is the reason why the ferromagnetism of $Zn_{0.91}Co_{0.05}Cu_{0.04}O$ decreases with the O-Ar ratio and increases with the increase of Cu^{+} ion concentration.

4 Conclusions

1) The doped Cu ions mainly occupied the Zn^{2+} sites with the mixed chemical valence of Cu^{+} and Cu^{2+}, which is determined by the sputtering O-Ar ratio.

2) The ferromagnetism was enhanced with the increase of Cu^{+} ion concentration. It indicates that p-type doping of Cu^{+} can improve the magnetic coupling between Co ions, which provides solid evidence for the bound magnetic polaron model.

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